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Thermoelectric behaviour of segregated conductive polymer composites with hybrid fillers of carbon nanotube and bismuth telluride

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ABSTRACT

A segregated polymer composite based on ultrahigh molecular weight polyethylene (UHMWPE), carbon nanotube (CNT) and p type bismuth telluride (Bi_2Te_3) was fabricated. Morphology observation confirmed the formation of a typical segregated conductive network of CNT/Bi_2Te_3 hybrids, in which the CNTs/Bi_2Te_3 hybrid fillers were only located at the interfaces of UHMWPE domains to form continuous conducting pathways. The segregated composite containing 2.6 vol% CNTs and 5.1 vol% Bi_2Te_3 exhibited an electrical conductivity of 45 S/m, thermal conductivity of 0.43 W/mK, Seebeck coefficient of 29 μV/K, and thermoelectric figure of merit $ZT=3\times10^{-5}$ at room temperature. This work implies that the formation of a segregated structure in polymer composites demonstrates a new strategy to develop polymer-based thermoelectric materials.

1. Introduction

The finite supply of carbon-based fossil fuels and the public panic on nuclear energy promote the development of affordable, renewable, and clean energy on a global scale [1]. Thermoelectric materials can directly convert abundant industrial heat waste to electricity, which possess a particular interest in the potentially viable energy resources [2,3]. The performance of thermoelectric devices is evaluated by a dimensionless quantity called the Figure of merit ZT [1]

$$ZT=\frac{S^2\sigma T}{\lambda} \tag{1}$$

where S is the Seebeck coefficient, σ is the electrical conductivity, λ denotes the thermal conductivity, and T is the absolute temperature. Thus, a desirable thermoelectric device requires a high Seebeck coefficient to enhance thermoelectricity, high electrical conductivity to minimize Joule heating, and low thermal conductivity to maintain large temperature gradient [4].

Most ongoing researches of thermoelectric devices are based on inorganic semicondutors, conducting oxide, and metal alloys [5–7]. Despite their high efficiency on harvesting electricity from heat waste, the typical thermoelectric devices are relatively expensive, toxic, and difficult to process [4]. Conductive polymer composites containing insulating polymer matrices and conducting fillers have been studied as inexpensive, lightweight, and more environmentally friendly alternatives to common thermoelectric devices [8–10]. Yu et al. fabricated a carbon nanotube (CNT)/poly (vinyl acetate) composite with a segregated structure and a relatively high ZT value over 0.006 was obtained with 20 wt% CNTs at room temperature [4]. Kim et al. achieved a maximum ZT of ~0.02 at room temperature for 35 wt% CNT-filled segregated polymer composites by adding conducting polymers to reduce the contact resistance between CNTs [9].

Recently, we prepared a segregated conductive polymer composite based on CNTs and ultrahigh molecular weight polyethylene (UHMWPE), which exhibited high electrical conductivity and low thermal conductivty with ultralow percolation threshold [11]. Considering the aforementioned requirements, our segregated composites have significant potential applications to thermoelectric materials. In the current work, we attempted to fabricate the thermoelectric polymer composites with a segregated structure. To improve their thermoelectric performance, we mixed Bi_2Te_3 particles with CNTs as hybrid fillers to form the segregated networks. Owing to the formation of perfect segregated networks of hybrid fillers, the electrical conductivity and Seebeck coefficient

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were dramatically enhanced, while the thermal conductivity almost remained independent to the hybrid filler concentration.

2. Experimental procedure

UHMWPE, a product from Beijing No.2 Auxiliary Agent Factory, Beijing, China, had the following properties: density of 0.94 g/cm^3, volume resistivity of 10^{17} Ω cm, and molecular weight of 6×10^6 g/mol. Multi-wall CNTs (20–40 nm diameter, 10–20 μm length) were supplied by Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). P type Bi_2Te_3 particles with an average diameter of ~3 μm and density of ~7.8 g/cm^3 were obtained from Chengdu Hanpu Co. Ltd. (Chengdu, China). The preparation of the segregated composites is schematically depicted in Fig. 1. Initially, the CNTs were suspended in ethanol and subjected to ultrasonication for 30 min to obtain a homogeneous suspension. After mixing with UHMWPE and Bi_2Te_3 particles in an ethanol system under ultrasonication and stirring for 1 h, the ethanol of the mixture was evaporated at 60 °C. The stirring and ultrasonication were also applied to avoid the formation of CNT and Bi_2Te_3 aggregates. After the solvent evaporating, only UHMWPE granules decorated with layers of CNTs and Bi_2Te_3 particles were left. Subsequently, the granules were compression-molded into $140 \times 50 \times 0.8$ mm^3 sheets at 200 °C for 5 min with a pressure of 10 MPa. The electrical conductivity and Seebeck coefficient were measured on a computer-aided apparatus using a dc four-probe method and differential voltage/temperature technique, respectively [12]. The specimens of optical microscopy were cut into films (~15 μm) using a microtome. The scanning electron microscopy (SEM) specimens were frozen in liquid nitrogen for 30 min, then quickly impact fractured. The freshly broken surfaces were observed by a field emission SEM (Inspect-F, FEI, Finland).

3. Results and discussion

Fig. 2 displays the surface of the CNT/Bi_2Te_3 hybrid fillers decorated UHMWPE granules, in which numerous CNT and Bi_2Te_3 particles overlapped each other. This morphology provides the prerequisite for the formation of segregated network at the interfaces of UHMWPE domains. The optical micrograph (Fig. 3a) of the segregated composites demonstrates the formation of a typical segregated conductive network, in which the conducting CNT/Bi_2Te_3 layers were predominantly located at the interfaces between UHMWPE granules throughout the composite. SEM micrographs were taken to observe the detailed microstructure of the conducting CNT/Bi_2Te_3 paths (Fig. 3b and c). The UHMWPE granules demonstrated a typical faceted structure (Fig. 3b), and adjacent individual UHMWPE granules formed very thin interfaces and held all the CNTs and Bi_2Te_3 particles (Fig. 3c). The formation of such a segregated conductive network can be explained from its fabrication process. During the hot press processing, the UHMWPE granules coated with CNTs and Bi_2Te_3 particles were almost not broken up, because of lack of shear and the gel state of UHMWPE domains [13]. Individual UHMWPE granules in the melt state, however, experienced plastic deformation under pressure to form polyhedrons. The CNT/Bi_2Te_3 hybrids decorated UHMWPE polyhedrons were well preserved during cooling process. Such a processing procedure, thus, resulted in a microstructure with a segregated network of CNT/Bi_2Te_3 hybrids. Moreover, the inset of Fig. 3a exhibits the high degree of flexibility of our segregated composite film.

Fig. 4a shows the electrical conductivity of the segregated composites with varying CNTs and Bi_2Te_3 content. The electrical conductivity decreased from 8.5 to 2.8 S/m with increasing Bi_2Te_3 loading from 10 to 30 wt% at a fixed CNT loading of 2 wt%. The reduced electrical conductivity was ascribed to that a high loading of Bi_2Te_3 particles occupied large volume at the interfaces between UHMWPE domains, causing the negative effect on the continuity of CNT conducting paths [14,15]. While for the 4 wt% CNT-filled composites, the electrical conductivty increased from 19.1 to 45.0 S/m, indicating that at a high CNT loading, the Bi_2Te_3 particles had a positive impact on the formation of CNT networks. This phenmonon might be attributed to the confinement of CNTs by larger exclusion volumes created by Bi_2Te_3 particles, which resulted in denser conducting CNT channels in the constrained environment. The thermal conductivity of the segreagated composites is shown in Fig. 4b. Despite the change of hybrid filler loading, the thermal conductivity almost remained constant around 0.4 W/mK. Owing to the thermal conductivity independence of Bi_2Te_3 loadings, the transport behaviors of segregated composites implies that the concentration of hybrid fillers could be increased without raising the composite thermal conductivity, which is particularly useful for tailoring thermoelectric behavior [4].

We further studied the effect of hybrid filler loading on the Seebeck coefficient. It is worth noting that the Seebeck coefficient of samples with 30 wt% Bi_2Te_3 loadings was ~34 and 29 μV/K for 2 and 4 wt% CNT loadings, respectively. These values were close to that obtained for intrinsically conductive polymers (e.g. polyaniline and polypyrrole) and metallic CNTs [4,16]. At relatively low Bi_2Te_3 loadings (10 and 20 wt%), the Seebeck coefficient of the segregated composites kept comparable values of ~13 μV/K. This result is due to the formation of a prefect segregated CNT/Bi_2Te_3 conductive networks at the interfaces between UHMWPE granules. *ZT* of the segregated composites was calculated at room temperature and presented in Fig. 4d. The 4 wt% CNTs/30 wt% Bi_2Te_3 hybrids led to the largest *ZT* (3×10^{-5}). Although the composite *ZT* was too low for commericial applications, we believe

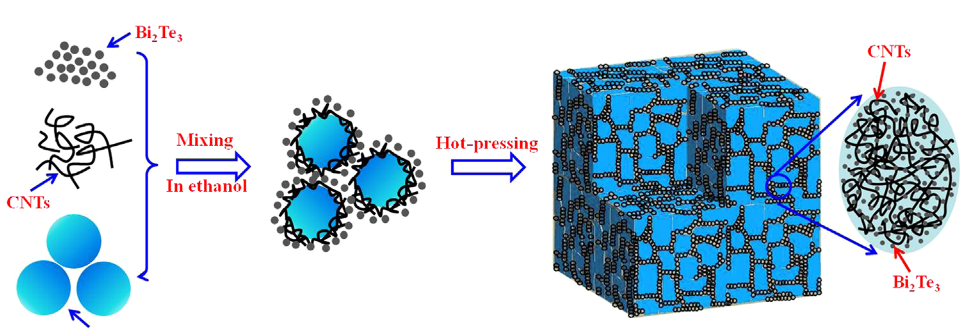

Fig. 1. Schematic showing the fabrication of our segregated composites.